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Signed William Morell

Dated 15 March 2005

**Patents Form 1/77**

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04FEB04 E870529-1 D02806
P01/7700 0.00-0402395.8 NONE

1. Your reference — CDK2158

2. Patent application number *(The Patent Office will fill in this part)* — 0402395.8

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

RHODIA CONSUMER SPECIALTIES LIMITED
Oak House
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- 3 FEB 2004

Patents ADP number *(if you know it)* 78703 22006

If the applicant is a corporate body, give the country/state of its incorporation — England

4. Title of the invention — SYNERGISTIC BIOCIDAL COMPOSITIONS

5. Name of your agent *(if you have one)* — Barker Brettell

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

138 Hagley Road
Edgbaston
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B16 9PW

Patents ADP number *(if you know it)* — 7442494002

6. Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months.

| Country | Priority application number *(if you know it)* | Date of Filing *(day/month/year)* |
|---|---|---|
| | | |

7. Divisionals, etc: Complete this section only if this application is a divisional application or resulted from an entitlement dispute (see note f)

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8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request? *Answer 'Yes' if:*
*a) any applicant named in part 3 is not an inventor, or*
*b) there is an inventor who is not named as an applicant, or*
*c) any named applicant is a corporate body.*
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YES

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| Description | 6 + 6 |
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| Priority documents | |
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| Statement of inventorship and right to grant of a patent *(Patents Form 7/77)* | |
| Request for preliminary examination *(Patents Form 9/77)* | |
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11. I/We request the grant of a patent on the basis of this application.

Signature: Barker Brettell — Date: 02 February 2004

12. Name and daytime telephone number of person to contact in the United Kingdom: Lucy P. Trueman — Tel: 0121 456 1364

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# SYNERGISTIC BIOCIDAL COMPOSITIONS

This invention relates to synergistic biocidal compositions.

The present invention is a selection invention relative to our published P.C.T. application WO 99/33345.

The said WO 99/33345 discloses synergistic biocidal compositions comprising "THP", a non-surfactant biopenetrant compatible with "THP" and optionally a surfactant.

The term "THP" is defined in WO 99/33345 as meaning **either** a tetrakis(hydroxyalkyl)phosphonium salt **or** a tris(hydroxyalkyl)phosphine. To avoid confusion we shall hereinafter refer to "THP salts" or "THP" respectively.

Examples of non-surfactant biopenetrants disclosed in the said WO 99/33345 include phosphonated derivatives of carboxylic acids, for example the phosphonated telomers disclosed in our published European applications EP-A-0 491 391 and EP-A-0 861 846.

Other non-surfactant biopenetrants disclosed in the said WO 99/33345 include a copolymer of N, N, N', N'-tetramethyl-1,2-diaminoethane with bis(2-chloroethyl)ether. This is commercially available under the trade name WSCP and will hereinafter be so referred to.

Where surfactants are used, examples disclosed in the said WO 99/33345 include sulphonated (anionic) surfactants and cationic surfactants such as those based on quaternary ammonium compounds, as well as non-ionic, amphoteric and semi-polar surfactants.

We have now unexpectedly found that where the biopenetrant is a phosphonic acid-tipped polymer or copolymer, it acts synergistically with a THP salt to considerably enhance the biocidal efficacy of the THP salt against both planktonic (free-swimming) and sessile (attached) bacteria.

Accordingly, the present invention provides a synergistic biocidal composition comprising

(i) a THP salt (as hereinbefore defined) and

(ii) a biopenetrant,

in which the biopenetrant comprises a polymer of an unsaturated carboxylic acid or a copolymer of an unsaturated carboxylic acid with a sulphonic acid, said polymer or copolymer being terminated by a mono-or di-phosphonated unsaturated carboxylic acid.

Preferably, the THP salt is tetrakis(hydroxymethyl)phosphonium sulphate (THPS). Other THP salts include the phosphite, bromide, fluoride, chloride, phosphate, carbonate, acetate, formate, citrate, borate, or silicate.

In accordance with preferred embodiments of the present invention, the biopenetrant may be a polyacrylate terminated with vinylphosphonic acid, (hereinafter "VPA end-capped polymer") or with vinylidene-1, 1-diphosphonic acid (hereinafter "VDPA end-capped polymer).

Alternatively, the biopenetrant may be an acrylate/sulphonate copolymer terminated with vinylidene-1, 1-diphosphonic acid (hereinafter "VDPA end-capped copolymer") or with vinylphosphonic acid (hereinafter "VPA end-capped co-polymer).

The preferred ratio of VPA polymer or VDPA copolymer to THP salt, in accordance with the present invention, is in the range 1 to 10%, preferably 2 to 8%, most preferably 3 to 5%, (based upon a 50% THP salt formulation).

We have found that the compositions according to the present invention are equally effective in reducing the level of general heterotrophic bacteria and of sulphate reducing bacteria in waters.

The present invention will be illustrated by way of the following examples.

In the examples, the various abbreviations have the following meaning:

| | |
|---|---|
| VPA polymer: | a vinylphosphonic acid-terminated polyacrylate of molecular weight about 4000 |
| VDPA copolymer: | a vinylidene-diphosphonic acid-terminated acrylate/sulphonate copolymer of molecular weight 6000-8000, typically about 7200. |
| GHB: | general heterotrophic bacteria |
| SRB: | sulphate reducing bacteria |
| WHO water: | World Health Organisation Standard Hardness Water (see TABLE I below) |
| SMOW water: | Standard Mean Ocean Water (see TABLE II below) |

THPS: a 50% aqueous solution of tetrakis(hydroxymethyl)phosphonium sulphate

WSCP: copolymer of N, N, N', N'-tetramethyl-1,2-diamino ethane and bis(2-chloroethyl)ether.

**TABLE I**

**WHO Standard Hardness Water**

| 1 litre contains: | |
|---|---|
| $CaCl_2$ (anhydrous) | 0.305 g |
| $MgCl_2.6H_2O$ | 0.139 g |

**TABLE II**

**Standard Mean Ocean Water**

| 5 litres contain: | |
|---|---|
| NaCl | 122.65 g |
| $MgCl_2.6H_2O$ | 55.52 g |
| $Na_2SO_4$ | 20.45 g |
| $CaCl_2.2H_2O$ | 7.69 g |
| KCl | 3.48 g |
| $NaHCO_3$ | 1.00 g |
| KBr | 0.50g |
| pH adjusted to 8.2 by means of 0.1N NaOH | |

**Example 1**

**Quantitative Suspension Test (Planktonic Bacteria) in WHO water**

| Test Product | Log Reduction of General Heterotrophic Bacteria (based upon 50ppm ai THPS) | |
|---|---|---|
| | 1 hour contact period | 3 hour contact |
| Control | 0 | 0 |
| Unformulated THPS | 1 | 5.8 |
| THPS/VPA polymer* | 7.4 | Total kill |
| THPS/VDPA polymer* | 7.4 | Total kill |
| THPS/0.7% WSCP | 3.7 | 7.4 |

**Example 2**

**Quantitative Suspension Test in De inking water**

| Test Product | Log reduction values for 75ppm ai THPS/3 hour contact | |
|---|---|---|
| | **GHB** | **SRB** |
| Control | 0 | 0 |
| Unformulated THPS | 3.8 | 3 |
| THPS/VPA polymer* | 5.1 | 3 |

**Example 3**

**Biofilm (sessile) tests: freshwater (WHO)**

| Test Product | Viable bacteria (GHB) after 75ppm ai THPS dosed for 3 hours |
|---|---|
| Control | $1x10^5$ |
| Unformulated THPS | $1x10^5$ |
| THPS/VPA polymer* | $1x10^2$ |
| THPS/VDPA polymer* | $<10$ |
| THPS/2% sulphonated surfactant (a) | $1x10^3$ |

**Example 4**

**Biofilm tests: seawater (SMOW)**

| Test Product | Viable bacteria after 75ppm ai THPS dosed for 3 hours | |
|---|---|---|
| | **GHB** | **SRB** |
| Control | $1x10^4$ | $1x10^6$ |
| Unformulated THPS | $1x10^2$ | $1x10^4$ |
| THPS/VPA polymer* | $<10$ | $<10$ |
| THPS/VDPA polymer* | $1x10^2$ | $1x10^2$ |
| THPS/5% quaternary ammonium compound(b) | $1x10^2$ | $1x10^3$ |

*In each case, the ratio of THPS to "polymer" was 50% a.i. THPS to 5% "polymer", the "polymer" comprising 25% solids as the sodium salt.

(a) A di-sodium salt of a mixed mono- and di-alkyl disulphonated diphenyl oxide, available as DOWFAX® 2A1.

(b) An alkyl dimethyl benzyl ammonium chloride, available as EMPIGEN®BAC 50.